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(54) CORROSION-RESISTANT RARE EARTH MAGNET AND MANUFACTURE THEREOF

(57)Abstract:

PURPOSE: To provide a corrosion-resistant rare-earth magnet whose surface is chemically stable in various kinds of atmosphere.

CONSTITUTION: A rare-earth magnet is subjected to fluorinating treatment in a fluorine group gas atmosphere or a fluorine gas-contained atmosphere, thereby forming a mixture which comprises an RF<sub>3</sub> compound which is stabilized to corrosion resistance or ROxF<sub>y</sub> compound or both compounds on a front surface layer of the rare-earth magnet. It is also possible to enhance the corrosion resistance of a raw-material of the rare-earth magnet dramatically by performing a specified heat treatment.

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(54)【発明の名称】 耐食性のすぐれた希土類磁石及びその製造方法

(57)【要約】

【目的】 種々の雰囲気に対して化学的に安定した表面を有し、希土類磁石素材そのものの耐食性を向上させることが可能な耐食性のすぐれた希土類磁石及びその製造方法の提供。

【構成】 希土類磁石にフッ素系ガス雰囲気中もしくはフッ素系ガスを含有する雰囲気中においてフッ素化処理を施して、希土類磁石の表層部に耐食性に対して安定な $RF_3$ 化合物または $ROXFY$ 化合物あるいはその両化合物からなる混合物を形成させ、あるいはさらに所要の熱処理を施すことにより、希土類磁石の素材そのものの耐食性を大幅に向上させることができる。

## 【特許請求の範囲】

【請求項 1】 希土類磁石（希土類元素 R のうち少なくとも 1 種以上含有）の表層部に  $RF_3$  化合物または  $ROXFY$  化合物あるいはその両化合物の混合物を有することを特徴とする耐食性のすぐれた希土類磁石。

【請求項 2】 希土類磁石（希土類元素 R のうち少なくとも 1 種以上含有）をフッ素系ガス雰囲気中またはフッ素系ガスを含有する雰囲気中でフッ素化処理して、該磁石の表層部に  $RF_3$  化合物または  $ROXFY$  化合物あるいはその両化合物の混合物を形成させることを特徴とする耐食性のすぐれた希土類磁石の製造方法。

【請求項 3】 希土類磁石（希土類元素 R のうち少なくとも 1 種以上含有）をフッ素系ガス雰囲気中またはフッ素系ガスを含有する雰囲気中でフッ素化処理して、該磁石の表層部に  $RF_3$  化合物または  $ROXFY$  化合物あるいはその両化合物の混合物を形成させたのち、さらに  $200^{\circ}\text{C} \sim 1200^{\circ}\text{C}$  の温度で熱処理を施すことを特徴とする耐食性のすぐれた希土類磁石の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】この発明は、高磁気特性を有しかつ耐食性にすぐれた希土類磁石に係り、磁石体表面にフッ素化処理を施すことにより、該磁石表層部に種々の雰囲気に対して安定な希土類とフッ素の化合物を形成させて、希土類磁石の素材自体の耐食性を著しく向上させた希土類磁石とその製造方法に関する。

## 【0002】

【従来の技術】今日、高性能永久磁石として代表的な R（Y を含む希土類元素の少なくとも 1 種以上）-Fe-B 系永久磁石（特公昭 61-34242 号等）は、三元系正方晶化合物の主相と R リッチ相を有する組織にて高磁石特性を発現し、 $iH_c$  が  $25\text{ kOe}$  以上、 $(BH)_{\text{max}}$  が  $45\text{ MGOe}$  以上と従来の高性能希土類コバルト磁石と比較しても、格段に高い磁石特性を発揮する。また、用途に応じ、選定された種々の磁石特性を発揮するよう、種々組成の R-Fe-B 系永久磁石が提案されている。

【0003】しかしながら、上記のすぐれた磁気特性を有する R-Fe-B 系永久磁石は、主成分として空気中で容易に酸化あるいは水酸化し、酸化物あるいは水酸化物を生成し易い希土類元素及び鉄を含有するため、R-Fe-B 系永久磁石を磁気回路に組込んだ場合に磁石表面に生成する酸化物あるいは水酸化物により、磁気回路の出力低下及び磁気回路間の磁性のばらつきを惹起し、また、表面に生成した酸化物の脱落による周辺機器への汚染の問題があった。

【0004】特に、R-Fe-B 系焼結永久磁石の場合は、その構成層が  $R_2Fe_{14}B$  相、R リッチ相、B リッチ相などから構成されており、そのうち、 $R_2Fe_{14}B$  相の粒界部に存在する R リッチ相は、R を多量に含有す

る相であるため極めて酸化あるいは水酸化され易く、磁石表面層において大気中の水分を吸収して体積膨張を起こし、 $R_2Fe_{14}B$  相の磁石表面層からの脱粒及び水酸化物そのものも脱落する問題があった。

【0005】そこで、上記の R-Fe-B 系永久磁石の耐食性を改善するため、磁石体表面に無電解めっき法あるいは電解めっき法により耐食性金属めっき層を被覆したり（特開昭 60-54406 号）、耐食性樹脂を浸漬法や塗布法にてコーティングしたり（特開昭 60-63901 号）、気相成膜法にて Al 等の耐食性金属、合金被膜を形成したり（特開昭 61-150201 号）、耐食性金属薄片を含む樹脂層を被着形成したり（特開昭 63-166944 号）、さらには異種の耐食性被膜を積層形成する（特開平 1-152602 号）などの耐食性被膜を設ける技術が提案された。

## 【0006】

【発明が解決しようとする課題】しかし、無電解めっき法あるいは電解めっき法は、R-Fe-B 系永久磁石を酸性あるいはアルカリ性溶液中で処理する為、磁石表面が腐食され磁気特性の劣化およびばらつきを生じるばかりでなく、めっき被膜にピンホールが存在するため、塩水噴霧テストなどの過酷な試験に対しては十分な耐食性が得られない。特に、構成相として酸化され易い R リッチ相を含有する R-Fe-B 系焼結永久磁石においては、上述の無電解めっき法あるいは電解めっき法などのいわゆる湿式めっき法では、めっき処理時に使用する酸性溶剤やアルカリ溶剤により該 R リッチ相が優先的に腐食されて、その腐食部分から該溶剤が磁石体内部にまで侵入するため、磁石体表面にめっき層を被覆しても、磁石体内部に残留する溶剤が R リッチ相を腐食し続け、最終的には内部腐食により、磁石体そのものが崩壊するといった問題があった。

【0007】一方、耐食性樹脂を浸漬法や塗布法あるいは電着法でコーティングした場合、ピンホールは存在しないが、樹脂被膜の透水率が金属被膜と比較して大きいため十分な耐食性が得られない問題があった。すなわち、従来の耐食性被膜などの表面処理では、下地となる磁石素材の耐食性があまり考慮されていないため、上記のような問題を引き起こすのである。そこで、上述のような種々の表面処理を施す前に、予め磁石素材に種々の添加元素、例えば耐食性にすぐれる Co、Ni、Al 等を添加して磁石素材そのものの耐食性を向上させる方法も提案されているが、上記の添加元素は、耐食性の効果を得るためには多量の添加が必要となり、そのために磁気特性が劣化したり、また、コストが高くなるなどの問題があった。

【0008】この発明は、上述の種々の問題を解決することを目的に、具体的には、種々の雰囲気に対して化学的に安定した表面を有し、希土類磁石素材そのものの耐食性を向上させることが可能な耐食性のすぐれた希土類

磁石及びその製造方法の提供を目的としている。

#### 【0009】

【課題を解決するための手段】発明者は、公知組成の各種希土類磁石素材自体の耐食性を向上させる磁石表層について検討し、磁石表層を種々の雰囲気に対し安定な化合物に変化させることに着目して、表面処理方法について種々検討した結果、フッ素化処理にて希土類(R)とフッ素(F)の化合物、すなわち、磁石の表層部に $RF_3$ 化合物または $RO_xF_y$ 化合物あるいはその両化合物の混合物を生成させると、磁石素材自体の耐食性を著しく向上させることが可能であることを知見し、この発明を完成した。すなわち、この発明は、希土類磁石の表層部に $RF_3$ 化合物または $RO_xF_y$ 化合物あるいはその両化合物の混合物を有することを特徴とする耐食性のすぐれた希土類磁石である。

【0010】また、この発明は、希土類磁石(希土類元素Rのうち少なくとも1種以上含有)をフッ素系ガス雰囲気中またはフッ素系ガスを含有する雰囲気中でフッ素化処理して、該磁石の表層部に $RF_3$ 化合物または $RO_xF_y$ 化合物あるいはその両化合物の混合物を形成させ、あるいはさらに $200^\circ\text{C} \sim 1200^\circ\text{C}$ の温度で熱処理を施すことを特徴とする耐食性のすぐれた希土類磁石の製造方法である。

#### 【0011】希土類磁石

この発明において、希土類磁石としては、Yを含む希土類元素Rを少なくとも1種以上含有する公知組成のあらゆる希土類磁石を対象とし、また磁石形態としても、公知の焼結磁石をはじめとして、鑄造磁石、圧延磁石、ボンド磁石などあらゆる形態を対象とし、あるいはさらにボンド磁石用の原料粉末など、あらゆる組成、製造方法で得られる磁石、またはそれらの原料粉末などに適用することができる。特に希土類磁石が、R、Fe (Feの一部をCo等の遷移金属元素で置換することができる)、B(ボロン)を主成分とする $R-Fe-B$ 永久磁石材料である場合には、この発明による効果が顕著に得られる。すなわち、上記の種々の希土類磁石を構成する構成相に少なくとも $R_2T_{14}B$ 相を有する希土類磁石、あるいは少なくとも $R_2T_{14}B$ 相及びRリッチ相を有する希土類磁石であれば、この発明のフッ素化処理を行なうことにより、耐食性向上の効果が期待できる。なお、Rリッチ相とは、希土類元素と遷移金属元素との化合物、または、希土類元素と遷移金属元素に一部半金属元素等が含まれる化合物で、希土類元素の量が遷移金属元素など希土類元素以外の量よりも多く含有されるものいう。この発明によるフッ素化処理に効果がある化合物としては、 $R_3TM$ 、 $RTM_5$ 、 $R_2TM_7$ 、 $RTM_3$ 、 $RTM_2$ 、 $R_2TM_3$ 、 $R_2TM_{17}$ 、 $R_5TM_{19}$ 、 $Dy_6Fe_2$ 、 $RTM$ 、 $R_2TM_{14}B$ 、 $R_{1.11}TM_4B_4$ (TMは遷移金属元素のうち少なくとも一種)などである。

#### 【0012】表層化合物

この発明において、希土類磁石の表層部に形成させる $RF_3$ 化合物または $RO_xF_y$ 化合物あるいはその両化合物の混合物は、それぞれが極めて安定な化合物であり、各化合物中のRは水分などと容易には反応しない。なお、上記の $RO_xF_y$ は、X、Yの各々の値が $0 < X < 1.5$ でかつ $2X + Y = 3$ を満足する化合物である。上記の化合物は、希土類磁石を構成する $R_2T_{14}B$ 相やRリッチ相を後述するフッ素化処理することにより $RF_3$ 化合物や $RO_xF_y$ 化合物あるいはその両化合物の混合物を形成する。この発明において、希土類磁石の表層部に形成させる $RF_3$ 化合物または $RO_xF_y$ 化合物あるいはその両化合物の混合物の形成厚みは、フッ素系ガスの雰囲気、フッ素化処理時間、フッ素化処理温度、フッ素化処理後の熱処理条件などを変化させることにより、自由にコントロールすることができ、その厚みが極めて僅かでも耐食性に対する効果が期待できるが、形成厚みを厚くするに従いフッ素化処理に要する時間が長くなり工業的規模での量産性が低下し、また磁気特性が劣化する傾向があるので、該化合物の形成厚みは $500\mu\text{m}$ 以下が好ましく、さらに工業的規模の量産性や耐食性に対する信頼性を考慮すると $1\mu\text{m} \sim 100\mu\text{m}$ がさらに好ましい範囲である。

【0013】この発明による表層部に $RF_3$ 化合物または $RO_xF_y$ 化合物あるいはその両化合物の混合物を有する希土類磁石はそれだけでも十分な耐食性を有するが、例えば、極めて苛酷な環境下で本希土類磁石を使用する場合など、なお一層の高耐食性が要求される場合は、公知の表面処理方法により、希土類磁石を金属、合金、樹脂などで被覆することもできる。公知の表面処理方法としては、金属、合金、樹脂等やまたそれらに各種添加物を混合したものなどを、電解めっき法、無電解めっき法、電着塗装法、スプレー塗装法、浸漬法、気相成膜法等により被覆するものである。また、例えば、めっき法により金属等を被覆したのち、さらに樹脂で被覆したり、気相成膜法により金属を被着させたのち、クロム酸塩処理を行なうなど、公知の表面処理材質および表面処理方法を種々組み合わせて被覆することもできる。

#### 【0014】フッ素化処理

この発明において、フッ素化処理は、例えば、希土類磁石をフッ素系ガス雰囲気中またはフッ素系ガスを含有する雰囲気中に晒すだけの簡単な方法にて行なうことができる。また、反応を促進させるために、予め表面を加工するか、または加工後熱処理を施した希土類磁石を、吸排気できる容器内に入れ、容器内を一旦真空状態にした後、フッ素系ガスを容器内へ所定圧力まで導入し、所定温度で所要時間保持したり、またフッ素系ガスを流気させた容器内に希土類磁石を挿入することによりフッ素化処理が行なえる。また、プラズマ処理によるフッ素化処理を行なうこともでき、例えば、フッ素系ガス雰囲気中またはフッ素系ガスを含有する雰囲気(不活性ガスとフ

ッ素系ガスの混合ガス) 中でプラズマ処理を行なう方法、酸素とフッ素系ガスとの混合ガス雰囲気中でプラズマ処理を行なう方法、酸素雰囲気中でプラズマ処理を行なった後フッ素系ガス雰囲気中でプラズマ処理を行なう方法、フッ素系ガス雰囲気中でプラズマ処理を行なった後酸素雰囲気中でプラズマ処理を行なう方法のうちいずれの方法でも処理可能である。この発明において、フッ素化処理に用いるフッ素系ガスとしては、 $F_2$ 、 $NF_3$ 、 $N_2F_4$ 、 $N_2F_2$ 、 $NOF$ 、 $NO_2F$ 、 $HF$ 、 $CF_4$ 、 $CHF_3$ 、 $CH_2F_2$ 、 $C_2F_6$ 、 $C_3F_8$ 、 $SiF_4$ 、 $SF_6$ 、 $OF_2$ 、 $BF_3$ 、 $PF_3$ 、 $PF_5$ 、 $ClF_3$ 、 $WF_6$ 、 $MoF_6$  等を用いることができ、また、フッ素系ガスとその他のガスとの混合ガス、例えばフッ素系ガスと窒素ガス、あるいはフッ素系ガスと酸素ガスなどとを混合したガスでも有効である。この発明によるフッ素化処理は、室温でも行なえるが、希土類磁石とフッ素系ガスとの反応を促進させるために、希土類磁石を所要の温度に加熱することも有効な手段である。しかし、フッ素化処理温度が高すぎると、希土類磁石とフッ素系ガスとの反応が急激に進行しすぎて、希土類磁石の表層部に形成する $RF_3$ 化合物または $ROXFY$ 化合物あるいはその両化合物の混合物の形成厚みを制御できないため、フッ素化処理は約 $600^{\circ}C$ 以下で行なうことが好ましい。この発明のフッ素化処理において、フッ素系ガスの圧力は使用するフッ素系ガスの種類によって異なるが、分圧が $10^{-8}mmHg$ 程度以上の雰囲気が好き、また、フッ素化処理時間は約1秒以上であれば充分であるが、フッ素系ガスの圧力及びフッ素化処理時間は、前述したフッ素系ガスの種類やそのガスに含有されるフッ素濃度、またフッ素化処理温度や処理する希土類磁石の組成や形態、さらには形成する化合物の厚みによって大きく変動するので、適宜最適条件を選定して行なうことが望ましい。

【0015】この発明によるフッ素化処理は、全工程を乾式処理にて行なうことを特徴とする。すなわち、湿式処理方式によるフッ素化処理では、磁石素材の溶出が避けられないが、乾式処理方式によるフッ素化処理では、フッ素系ガス(気相)と希土類磁石(固相)との気相-固相反応であることから、磁石素材の溶出はほとんどなく、磁石素材そのものの耐食性を向上させることができる。また、従来の電解めっきや無電解めっきなどのいわゆる湿式処理による耐食性被膜の如く、処理時の前処理に用いる酸性溶剤やアルカリ溶剤などの残留による磁石内部からの腐食などの問題を一扫できるうえ、従来の表面処理に比べても極めて優れた耐食性を発揮できる。さらに、フッ素系ガスの雰囲気、フッ素化処理時間、フッ素化処理温度、フッ素化処理後の熱処理条件などを変化させることにより、希土類磁石の表層に形成させる $RF_3$ 化合物または $ROXFY$ 化合物あるいはその両化合物の混合物の形成厚みを自由にコントロールすることができる。この発明におけるフッ素化処理は、上述の如くフッ

素系ガス雰囲気中またはフッ素系ガスを含有する雰囲気中に希土類磁石を晒す方法やプラズマ処理などの乾式処理で行なうことが最も好ましいが、例えば、フッ素系溶剤中やフッ素系溶剤を含有する溶液中に希土類磁石を浸漬するなどのいわゆる湿式処理によってもフッ素化を行なうことができる。しかし、湿式によるフッ素化処理においては、若干は磁石素材が溶出するので、フッ素系溶剤やフッ素系溶剤を含有する溶液の濃度を最適な濃度に維持して磁石素材の溶出を極力少なくすることが望ましい。

#### 【0016】熱処理

この発明において、フッ素化処理後に所要の熱処理を施すことにより、その機構は不明であるが、 $RF_3$ 化合物または $ROXFY$ 化合物あるいはその両化合物の混合物組織などの緻密化、安定化に寄与し、希土類磁石の耐食性をより一層向上させることができるため有効である。上記の熱処理温度は、 $200^{\circ}C$ 以下では $RF_3$ 化合物または $ROXFY$ 化合物あるいはその両化合物の混合物の緻密化、安定化の促進に多大な時間を要し、また $1200^{\circ}C$ を超えると希土類磁石が溶融してしまうため、好ましい熱処理温度は $200^{\circ}C \sim 1200^{\circ}C$ であり、また、熱処理時間及び熱処理雰囲気は、最適の条件を適宜選定して行なうことが好ましい。上記の熱処理を、予め時効処理を施した永久磁石に施す場合は、 $200^{\circ}C \sim$ 当該時効処理温度以下の範囲で熱処理を行なうことが好ましい。これは、熱処理が時効処理温度を超えると、事前に施した時効処理効果がなくなり、磁気特性が低下するためである。さらに、当該時効処理温度以上の熱処理を行なった後、時効処理を施したり、熱処理と同時に時効処理を行なうことも可能である。

#### 【0017】

【作用】この発明は、希土類磁石をフッ素系ガス雰囲気中またはフッ素系ガスを含有する雰囲気中に晒しフッ素化処理することにより、希土類磁石の表層に $RF_3$ 化合物または $ROXFY$ 化合物あるいはその両化合物の混合物からなる安定な化合物を形成させ、あるいはさらに所要の熱処理を施すことにより該化合物の緻密化、安定化を一層促進させて、希土類磁石の耐食性を著しく向上させることができる。また、この発明によるフッ素化処理は、フッ素系ガス(気相)と希土類磁石(固相)との気相-固相反応であるために、処理中に磁石素材の溶出がほとんどなく、さらに電解めっきや無電解めっきなどのいわゆる湿式処理による酸性溶剤やアルカリ溶剤などの残留の問題が解消できるため、特に表面処理を行なわなくともすぐれた耐食性が得られ、また表面処理する際の下地処理としてもすぐれた効果を発揮する。

#### 【0018】

##### 【実施例】

##### 実施例1

試料として、組成がNd31.5B1.15残部Fe(重量%)

からなるR-T-B系焼結永久磁石に全面研削加工を施した試料を、吸排気できる容器内に挿入し、該容器内を $10^{-5}$ mmHg以下まで真空排気したのち、 $F_2$ と $N_2$ の混合ガス(10% $F_2$ 、90% $N_2$ 、純度99.9%)を $10^{-2}$ mmHg容器内に導入し、10分間試料を放置するフッ素化処理を施して、磁石表層部に $RF_3$ 化合物および $ROXFY$ 化合物あるいはその両化合物の混合物を形成したこの発明による磁石を得た(試料No. 1)。上記試料に形成された化合物の厚みをEPMAにより測定したところ、化合物の形成厚みは約 $10\mu m$ であった。また、上記試料のP. C. T試験(温度 $125^\circ C$ 、湿度85%、圧力2atm)を12時間と120時間の条件で行ない、試験後の酸化による重量変化量の比較により耐食性を評価した。試験の結果を表1に示す。

#### 【0019】実施例2

実施例1と同組成のR-T-B系焼結永久磁石に加工を施した試料に、実施例1と同様なフッ素化処理を施したのち、 $10^{-5}$ mmHg以下まで真空排気したのち、該容器内を $400^\circ C$ の温度に加熱し60分保持した後、磁石表層部に $RF_3$ 化合物および $ROXFY$ 化合物あるいはその両化合物の混合物を形成したこの発明による磁石を得た(試料No. 2)。上記試料に形成された化合物の厚みをEPMAにより測定したところ、化合物の形成厚みは約 $10\mu m$ であった。また、上記試料に実施例1と同じP. C. T試験を行ない、試験後の酸化による重量変化量の比較により耐食性を評価した結果を表1に示す。

#### 【0020】実施例3

実施例1と同組成のR-T-B系焼結永久磁石に加工を施した試料を、吸排気できる容器内に挿入し、該容器内を $10^{-5}$ mmHg以下まで真空排気したのち、該容器内を $200^\circ C$ の温度に加熱し、さらに $NF_3$ (三フッ化窒素、純度99.9%)を $10^{-4}$ mmHg容器内に導入し、30分間試料を放置するフッ素化処理を施したのち、 $10^{-5}$ mmHg以下の真空雰囲気下で $400^\circ C$ 、60分の熱処理を施して、磁石表層部に $RF_3$ 化合物および $ROXFY$ 化合物あるいはその両化合物の混合物を形成したこの発明による磁石を得た(試料No. 3)。上記試料に形成された化合物の厚みをEPMAにより測定したところ、化合物の形成厚みは約 $5\mu m$ であった。また、上記試料に実施例1と同じP. C. T試験を行ない、試験結果を表1に示す。

#### 【0021】実施例4

実施例1と同組成のR-T-B系焼結永久磁石に加工を施した試料を、吸排気できる容器内に挿入し、該容器内を $10^{-5}$ mmHg以下まで真空排気したのち、該容器内を $400^\circ C$ の温度に加熱し、さらに $CF_4$ (四フッ化メタン、純度99.9%)を $10$ mmHg容器内に導入し、10分間試料を放置するフッ素化処理を施して、磁石表層部に $RF_3$ 化合物および $ROXFY$ 化合物あるいはその両化合物の混合物を形成したこの発明による磁石を得た(試料No. 4)。上記試料に形成された化合物の厚みをEPMAにより測定したところ、化合物の形成厚みは約 $20\mu m$ であった。また、上記試料に実施例1と同じP. C. T試験を行ない、試験結果を表1に示す。

#### 【0022】実施例5

実施例1と同組成のR-T-B系焼結永久磁石に加工を施したのち、 $500^\circ C$ 、60分の時効処理を施した試料を、吸排気できる容器内に挿入し、該容器内を $10^{-5}$ mmHg以下まで真空排気したのち、 $HF$ (フッ化水素、純度99.9%)を流気させた雰囲気中に1分間試料を放置するフッ素化処理を施したのち、 $10^{-5}$ mmHg以下の真空雰囲気下で $500^\circ C$ 、60分の熱処理を施して、磁石表層部に $RF_3$ 化合物および $ROXFY$ 化合物あるいはその両化合物の混合物を形成したこの発明による磁石を得た(試料No. 5)。上記試料に形成された化合物の厚みをEPMAにより測定したところ、化合物の形成厚みは約 $100\mu m$ であった。また、上記試料に実施例1と同じP. C. T試験を行ない、試験結果を表1に示す。

#### 【0023】比較例

実施例と同じ組成のR-T-B系焼結永久磁石に、焼結後加工を施しただけで、フッ素化処理を全く施さないもの(試料No. 6)、及び組成が $Nd_{31.5}B_{1.5}Co_{5.0}$ 残部Fe(重量%)からなりCoを添加して予め素材の耐食性を向上させたR-T-B系焼結永久磁石に、焼結後加工を施しただけでフッ素化処理を全く施さないもの(試料No. 7)とを得た。上記比較例の試料について実施例1と同じP. C. T試験を行ない、試験結果を表1に示す。

#### 【0024】

#### 【表1】

	試料No.	重量変化量 ( $\Delta/\text{cm}^2(\times 10^{-4})$ )	
		P.C.T試験 12時間後	P.C.T試験 120時間後
実施例	1	0.0	0.9
	2	0.0	0.0
	3	0.0	0.0
	4	0.0	0.5
	5	0.0	0.0
比較例	6	18.6	24.0
	7	2.5	4.7

【0025】表1から明らかなように、フッ素化処理を施さない磁石（試料No. 6）は、P. C. T試験のような厳しい環境下では、時間の経過とともに酸化が著しく進行し、重量の変化が激しい。また、Coの添加により予め素材の耐食性を向上させた磁石（試料No. 7）であっても、時間の経過とともに酸化が進行しており、耐食性が劣る。これに対して、フッ素化処理を施したこの発明による希土類磁石（試料No. 1～5）は、種々の条件でフッ素化処理を行ったいずれのものについても、極めて苛酷な状況下において酸化せずに、すぐれた耐食性を有していることがわかる。特に、フッ素化処理を施した後、熱処理を施した磁石（試料No. 2, 3, 5）は、P. C. T試験に寄る重量変化が全くなく、極めてすぐれた耐食性を有していることがわかる。これは、この発明によるフッ素化処理を施した希土類磁石の表層部に、水分等に対して極めて安定な $\text{RF}_3$ 化合物および $\text{ROxFY}$ 化合物あるいはその両化合物の混合物が形成されているためである。

【0026】また、実施例1によりフッ素系ガスを含有する雰囲気中にてフッ素化処理を施した磁石（試料No. 1）及び実施例2によりフッ素系ガスを含有する雰囲気中にてフッ素化処理を施した後、さらに熱処理を施した磁石（試料No. 2）の各々について、磁石表層部のX線回折（ターゲットに $\text{Cu-K}\alpha$ を使用）を行った。X線回折の結果をフッ素化処理を全く施さない未処理の磁石（試料No. 6）についての結果とともに図1に示す。なお、図1のAは試料No. 2の実施例2磁石、Bは試料No. 1の実施例1磁石、Cは未処理の磁石（試料No. 6）のX線回折の結果を示す。図1から

明らかなように、フッ素化処理を施さない未処理の磁石（試料No. 6）については、該磁石の構成層である $\text{Nd}_2\text{Fe}_{14}\text{B}$ 及びNdが存在していることがわかる。これらの $\text{Nd}_2\text{Fe}_{14}\text{B}$ 及びNdは先述の如く、非常に容易に酸化され易く、一旦酸化物が形成されるとそれらの酸化物は吸湿性であることから、磁石表面において容易に大気中の水分と反応して、体積膨張を起こし、 $\text{R}_2\text{Fe}_{14}\text{B}$ 相を初めとする磁石構成相の脱粒、脱落を引き起こすのである。一方、フッ素化処理を施したもの（試料No. 1）及びフッ素化処理後、熱処理を施したもの（試料No. 2）については、磁石表層部の前記のNdなどのほぼ全体が $\text{NdF}_3$ 及び $\text{NdOF}$ あるいはその両化合物の混合物を主体とする希土類元素とフッ素の化合物が存在していることがわかる。上記の如く、希土類磁石にフッ素化処理を施すか、あるいはフッ素化処理を施した後さらに熱処理をすることにより、希土類磁石構成相のうち、特に耐食性に悪影響を及ぼす希土類やその酸化物などを $\text{NdF}_3$ または $\text{NdOF}$ あるいはその両化合物の混合物を主体とする希土類元素とフッ素の化合物にすることができ、希土類磁石の素材そのものの耐食性を大幅に向上させることができる。

#### 【0027】

【発明の効果】この発明は、希土類磁石にフッ素系ガス雰囲気中もしくはフッ素系ガスを含有する雰囲気中においてフッ素化処理を施して、希土類磁石の表層部に耐食性に対して安定な $\text{RF}_3$ 化合物または $\text{ROxFY}$ 化合物あるいはその両化合物からなる混合物を形成させ、あるいはさらに所要の熱処理を施すことにより、希土類磁石の素材そのものの耐食性を大幅に向上させることができ

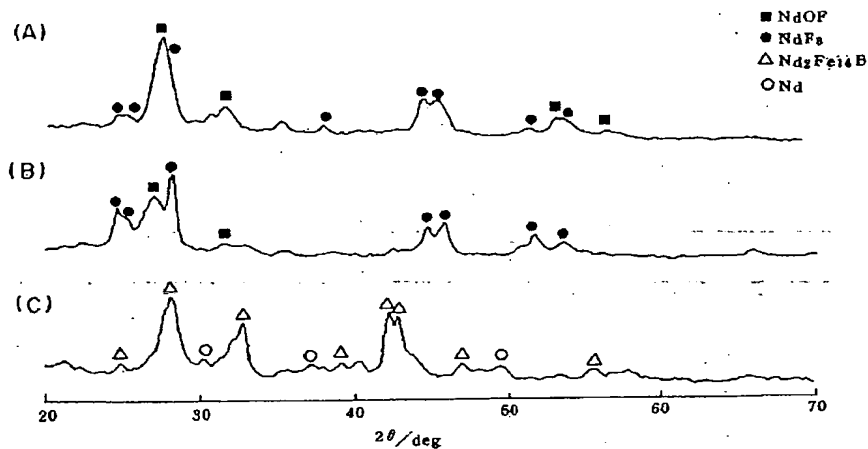
る。また、この発明によるフッ素化処理は、処理自体が非常に容易で、しかもフッ素系ガス（気相）と希土類磁石（固相）との気相-固相反応であるために、処理中に磁石素材の溶出がほとんどなく、さらに電解めっきや無電解めっきなどのいわゆる湿式処理による酸性溶剤や、アルカリ溶剤などの残留の問題が解消できるうえ、希土類磁石素材そのものの耐食性を向上できるため、表面処理する際の下地処理としてもすぐれた効果を発揮し、さ

らには、特に表面処理を行なわなくとも、苛酷な環境下で希土類磁石を使用することが可能となる。

【図面の簡単な説明】

【図1】磁石表層部のX線回折結果を示す回折パターン図であり、Aは試料No. 2の実施例2磁石、Bは試料No. 1の実施例1磁石、Cは未処理の磁石（試料No. 6）のX線回折の結果を示す。

【図1】



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## CLAIMS

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[Claim(s)]

[Claim 1] The rare earth magnet which excelled [ section / of a rare earth magnet (at least one or more sorts in rare earth elements R are contained) / surface ] in the corrosion resistance characterized by having RF3 compound, a ROXFY compound, or the mixture of both the compound.

[Claim 2] The manufacture approach of the outstanding rare earth magnet of the corrosion resistance which carries out fluorination processing of the rare earth magnet (at least one or more sorts in rare earth elements R are contained) in the ambient atmosphere containing the inside of a fluorine system gas ambient atmosphere, or fluorine system gas, and is characterized by making RF3 compound, a ROXFY compound, or the mixture of both the compound form in the surface section of this magnet.

[Claim 3] The manufacture approach of the outstanding rare earth magnet of the corrosion resistance characterize by heat-treat at the temperature of 200 more degrees C - 1200 degrees C after carry out fluorination processing of the rare earth magnet (at least one or more sorts in rare earth elements R be contain) in the ambient atmosphere containing the inside of a fluorine system gas ambient atmosphere, or fluorine system gas and make RF3 compound, a ROXFY compound, or the mixture of both the compound form in the surface section of this magnet.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] By starting the rare earth magnet which has high magnetic properties and was excellent in corrosion resistance, and performing fluorination processing to a magnet body surface, this invention makes the compound of stable rare earth and a fluorine form in this magnet surface section to various ambient atmospheres, and relates to the rare earth magnet which raised remarkably the corrosion resistance of the raw material of a rare earth magnet itself, and its manufacture approach.

[0002]

[Description of the Prior Art] even if R(at least one or more sorts of rare earth elements containing Y)-Fe-B system permanent magnets (JP,61-34242,B etc.) typical as a high performance permanent magnet discover a high magnet property in the organization which has the main phase and R rich phase of a ternary system tetragonal compound and iHc compares them with 25 or more kOes and the high performance rare earth cobalt magnet of the 45 or more MGOes and the former, they are boiled markedly and demonstrate a high magnet property today. [ max / (BH) ] Moreover, the R-Fe-B system permanent magnet of a presentation is variously proposed so that the selected various magnet properties may be demonstrated according to an application.

[0003] However, the R-Fe-B system permanent magnet which has the magnetic properties which were excellent in the above Since the rare earth elements and iron which oxidize or hydroxylate easily in air as a principal component, and are easy to generate an oxide or a hydroxide are contained, When a R-Fe-B system permanent magnet was built into a magnetic circuit, there was a problem of the contamination to the peripheral device by omission of the oxide which the loss of power of a magnetic circuit and magnetic dispersion between magnetic circuits were caused, and was generated on the front face with the oxide or hydroxide generated on a magnet front face.

[0004] Especially in the case of a R-Fe-B system sintering permanent magnet R rich phase which the configuration layer consists of R<sub>2</sub>Fe<sub>14</sub>B phase, an R rich phase, a B rich phase, etc., among those exists in the grain boundary section of R<sub>2</sub>Fe<sub>14</sub>B phase Since it was the phase which contains R so much, it oxidized or was very easy to hydroxylate, and there was a problem from which the moisture in atmospheric air is absorbed in a magnet surface layer, and degreasing from the magnet surface layer of a lifting and R<sub>2</sub>Fe<sub>14</sub>B phase and the hydroxide itself are omitted in cubical expansion.

[0005] In order to improve the corrosion resistance of the above-mentioned R-Fe-B system permanent magnet, cover a corrosion-resistant metal plating layer with a nonelectrolytic plating method or the electrolysis galvanizing method to a magnet body surface, or Then, (JP,60-54406,A), Coat corrosion-resistant resin with dip coating or the applying method, or (JP,60-63901,A), Form corrosion-resistant metals, such as aluminum, and an alloy coat by the gaseous-phase forming-membranes method, or (JP,61-150201,A), Covering formation of the resin layer containing corrosion-resistant foil was carried out, and the technique of preparing a corrosion-resistant coat, such as carrying out laminating formation of (JP,63-166944,A) and the corrosion-resistant, coat further of a different kind (JP,1-152602,A), was proposed.

[0006]

[Problem(s) to be Solved by the Invention] However, since it not only produces degradation and dispersion of magnetic properties, but a magnet front face is corroded and a pinhole exists in a plating coat in order that a nonelectrolytic plating method or the electrolysis galvanizing method may process a R-Fe-B system permanent magnet in acidity or an alkaline solution, sufficient corrosion resistance is not acquired to the severe trial of a salt fog test etc. In the R-Fe-B system sintering permanent magnet containing R rich phase which is especially easy to oxidize as a configuration phase By the so-called wet galvanizing methods, such as an above-mentioned nonelectrolytic plating method or the electrolysis galvanizing method Since this R rich phase is preferentially corroded by the acid solvent and alkali solvent which are used at the time of plating processing and this solvent trespasses even upon the interior of a magnet object from the corrosion part, Even if it covered the plating layer to the magnet body surface, the solvent which remains inside a magnet object continued corroding R rich phase, and there was a problem that the magnet object itself collapsed, by internal corrosion eventually.

[0007] On the other hand, although the pinhole did not exist when corrosion-resistant resin was coated with dip coating, the applying method, or an electrodeposition process, there was a problem from which sufficient corrosion resistance is not acquired for the coefficient of water permeability of a resin coat since it is large as compared with a metal coat. That is, in surface treatment, such as the conventional corrosion-resistant coat, since the corrosion resistance of the magnet raw material used as a substrate is seldom taken into consideration, the above problems are caused. Then, although the approach of adding beforehand Co, nickel, aluminum, etc. which are excellent in various alloying elements, for example, corrosion resistance, for a magnet raw material, and raising the corrosion resistance of the magnet raw material itself was also proposed before performing the above various surface treatment, in order to acquire corrosion resistance effectiveness, a lot of addition was needed, therefore magnetic properties deteriorated and the above-mentioned alloying element had problems, like cost becomes high.

[0008] This invention specifically has the front face chemically stabilized to various ambient atmospheres for the purpose of solving above-mentioned various problems, and aims at offer of the corrosion resistance outstanding rare earth magnet which can raise the corrosion resistance of the rare earth magnet raw material itself, and its manufacture approach.

[0009]

[Means for Solving the Problem] An artificer examines the magnet surface which raises the corrosion resistance of the various rare earth magnet raw material of a well-known presentation itself, and it notes changing a magnet surface to a stable compound to various ambient atmospheres. If the compound of rare earth (R) and a fluorine (F), i.e., the magnetic surface section, is made to generate RF<sub>3</sub> compound, a ROXFY compound, or the mixture of both the compound by fluorination processing as a result of examining many things about the surface treatment approach The knowledge of it being possible to raise the corrosion resistance of the magnet raw material itself remarkably was carried out, and this invention was completed. That is, this invention is the rare earth magnet which excelled [ section / of a rare earth magnet / surface ] in the corrosion resistance characterized by having RF<sub>3</sub> compound, a ROXFY compound, or the mixture of both that compound.

[0010] Moreover, this invention be the manufacture approach of the outstanding rare earth magnet of the corrosion resistance characterize by carry out fluorination processing of the rare earth magnet (at least one or more sorts in rare earth elements R be contain) in the ambient atmosphere containing the inside of a fluorine system gas ambient atmosphere, or fluorine system gas, and make RF<sub>3</sub> compound, a ROXFY compound, or the mixture of both that compound form in the surface section of this magnet, or heat-treat at the temperature of 200 more degrees C - 1200 degrees C.

[0011] In invention of \*\*\*\*\* as a rare earth magnet It is aimed at all the rare earth magnets of the well-known presentation containing at least one or more sorts of rare earth elements R containing Y. Also as a magnet gestalt It is applicable to the magnets obtained by all presentations, such as raw material powder further for bond magnets, and the manufacture approach, or those raw material powder for all gestalten, such as casting magnets including a well-known sintered magnet, a cold workable magnet, and a bond magnet. When it is the R-Fe-B permanent magnet ingredient with which especially a

rare earth magnet carries out a principal component for R, Fe (transition-metals elements, such as Co, can permute a part of Fe), and B (boron), the effectiveness by this invention is acquired notably. That is, if it is the rare earth magnet which has R2T14 B phase at least in the configuration phase which constitutes the above-mentioned various rare earth magnets, or the rare earth magnet which has R2T14 B phase and R rich phase at least, the effectiveness of corrosion-resistant improvement is expectable by performing fluorination processing of this invention. In addition, R rich phase is the compound of rare earth elements and a transition-metals element, or the compound with which metalloid element etc. is contained in rare earth elements and a transition-metals element in part, and rather than amounts other than rare earth elements, such as a transition-metals element, many amounts of rare earth elements contain and say. as the compound which has effectiveness in the fluorination processing by this invention -- R3 -- TM, RTM5, R2TM7, RTM3 and RTM2, R2TM3, R2TM17, and R5 -- TM19 and Dy6 -- it is Fe2, RTM, R2TM14B, and R1.11TM4 B4 (TM is a kind at least among transition-metals elements) etc.

[0012] In invention of surface \*\*\*\*\*, RF3 compound made to form in the surface section of a rare earth magnet, a ROXFY compound, or the mixture of both the compound is a compound with very stable each, and R in each compound does not react as easily as moisture etc. In addition, above ROXFY (s) are X and a compound with which the values of Y are  $0 < X < 1.5$ , and it is satisfied of  $2X + Y = 3$ . The above-mentioned compound forms RF3 compound, a ROXFY compound, or the mixture of both the compound by [ which mention later the R2T14 B phase which constitutes a rare earth magnet, and R rich phase ] carrying out fluorination processing. In this invention, the formation thickness of RF3 compound made to form in the surface section of a rare earth magnet, a ROXFY compound, or the mixture of both that compound Although the effectiveness over corrosion resistance is expectable even if it can control freely and the thickness is very slight by changing the ambient atmosphere of fluorine system gas, the fluorination processing time, fluorination processing temperature, the heat treatment conditions after fluorination processing, etc. Since there is an inclination for the time amount which fluorination processing takes to become long, and for the mass production nature in industrial magnitude to fall, and for magnetic properties to deteriorate as formation thickness is thickened When the formation thickness of this compound has desirable 500 micrometers or less and the dependability over the mass production nature of industrial magnitude or corrosion resistance is further taken into consideration, 1 micrometer - 100 micrometers are the still more desirable range.

[0013] Although the rare earth magnet which has RF3 compound, a ROXFY compound, or the mixture of both that compound in the surface section by this invention has sufficient corrosion resistance but [ so ], when using this rare earth magnet under a for example very cruel environment and still much more high corrosion resistance is required, it can also cover a rare earth magnet with the well-known surface treatment approach by the metal, the alloy, resin, etc. As the well-known surface treatment approach, a metal, an alloy, resin, etc. the thing that mixed various additives to them again are covered with the electrolysis galvanizing method, a nonelectrolytic plating method, electropainting, the spraying method, dip coating, the gaseous-phase forming-membranes method, etc. Moreover, after covering with resin further, for example after covering a metal etc. with the galvanizing method, or making a metal put by the gaseous-phase forming-membranes method, it can also cover combining various well-known surface treatment construction material and the surface treatment approaches, such as performing chromate treatment.

[0014] fluorination \*\*\*\* -- in this invention, fluorination processing can be performed by the easy method of exposing a rare earth magnet into the ambient atmosphere containing the inside of a fluorine system gas ambient atmosphere, or fluorine system gas. Moreover, in order to promote a reaction, once putting in the rare earth magnet which processed the front face beforehand or performed the processing postheat treatment in the container which can carry out pumping and making the inside of a container into a vacua, fluorine system gas is introduced to a predetermined pressure into a container, and fluorination processing can be performed by carrying out duration maintenance and inserting a rare earth magnet into the container made to \*\*\*\* fluorine system gas at predetermined temperature. Moreover, fluorination processing by plasma treatment can also be performed. For example, the method of

performing plasma treatment in the ambient atmosphere (mixed gas of inert gas and fluorine system gas) containing the inside of a fluorine system gas ambient atmosphere, or fluorine system gas, How to perform plasma treatment in the mixed-gas ambient atmosphere of oxygen and fluorine system gas, After performing plasma treatment in the approach of performing plasma treatment in a fluorine system gas ambient atmosphere after performing plasma treatment in an oxygen ambient atmosphere, and a fluorine system gas ambient atmosphere, it can process by any approach among the approaches of performing plasma treatment in an oxygen ambient atmosphere. In this invention, as fluorine system gas used for fluorination processing F<sub>2</sub>, NF<sub>3</sub>, N<sub>2</sub>F<sub>4</sub>, and N<sub>2</sub>F -- 2, NOF, NO<sub>2</sub>F, HF, CF<sub>4</sub> and CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, SiF<sub>4</sub>, SF<sub>6</sub>, OF<sub>2</sub> and BF<sub>3</sub>, PF<sub>3</sub>, PF<sub>5</sub>, and ClF<sub>3</sub>, WF<sub>6</sub> and MoF<sub>6</sub> It can use. etc. -- It is effective also by the gas which mixed mixed gas, for example, the fluorine system gas, nitrogen gas or fluorine system gas, oxygen gas, etc. of fluorine system gas and other gas. Fluorination processing by this invention can be performed at a room temperature, and in order to promote the reaction of a rare earth magnet and fluorine system gas, it is also an effective means to heat a rare earth magnet to necessary temperature. However, if fluorination processing temperature is too high, since the formation thickness of RF<sub>3</sub> compound which the reaction of a rare earth magnet and fluorine system gas advances too much rapidly, and is formed in the surface section of a rare earth magnet, a ROXFY compound, or the mixture of both the compound is uncontrollable, it is desirable to perform fluorination processing below about 600 degrees C. Although the pressure of fluorine system gas changes in fluorination processing of this invention with classes of fluorine system gas to be used Although the ambient atmosphere more than 10-8mmHg extent has a desirable partial pressure, and the fluorination processing time is enough if it is about 1 seconds or more The pressure and the fluorination processing time of fluorine system gas Since it changes sharply with the presentation of the fluorine concentration contained in the class of fluorine system gas mentioned above, or its gas and fluorination processing temperature, or the rare earth magnet to process, or the thickness of a gestalt and the compound formed further, it is desirable to carry out by selecting optimum conditions suitably.

[0015] It is characterized by the fluorination processing by this invention performing all processes by dry type processing. That is, by fluorination processing by the wet process method, although elution of a magnet raw material is not avoided, since it is the gaseous-phase-solid phase reaction of fluorine system gas (gaseous phase) and a rare earth magnet (solid phase), there is almost no elution of a magnet raw material, and it can raise the corrosion resistance of the magnet raw material itself by the fluorination processing by dry type mode of processing. Moreover, in being able to sweep away problems, such as corrosion from the interior of a magnet by the residual of the acid solvent used for pretreatment at the time of processing like the corrosion-resistant coat by the so-called wet processes, such as the conventional electrolysis plating and nonelectrolytic plating, an alkali solvent, etc., even if compared with the conventional surface treatment, the extremely excellent corrosion resistance can be demonstrated. Furthermore, the formation thickness of RF<sub>3</sub> compound made to form in the surface of a rare earth magnet, a ROXFY compound, or the mixture of both the compound is freely controllable by changing the ambient atmosphere of fluorine system gas, the fluorination processing time, fluorination processing temperature, the heat treatment conditions after fluorination processing, etc. Although it is most desirable to carry out by dry type processing of an approach, plasma treatment, etc. in which a rare earth magnet is exposed into the ambient atmosphere which contains the inside of a fluorine system gas ambient atmosphere or fluorine system gas like \*\*\*\* as for the fluorination processing in this invention, it can be fluorinated also by the so-called wet process of a rare earth magnet being immersed for example, into the solution containing the inside of a fluorine system solvent, or a fluorine system solvent. However, in the fluorination processing by wet, since a magnet raw material is eluted a little, it is desirable to maintain the concentration of the solution containing a fluorine system solvent or a fluorine system solvent to the optimal concentration, and to lessen elution of a magnet raw material as much as possible.

[0016] \*\*\*\*\* -- in this invention, although that device is unknown by performing necessary heat treatment after fluorination processing, since it can contribute to eburnation, such as RF<sub>3</sub> compound, a ROXFY compound, or a mixture organization of both that compound, and stabilization and the

corrosion resistance of a rare earth magnet can be raised further, it is effective. Since a rare earth magnet will fuse if the above-mentioned heat treatment temperature requires time amount great to acceleration of the eburnation of RF3 compound, a ROXFY compound, or the mixture of both the compound, and stabilization below 200 degrees C and exceeds 1200 degrees C, desirable heat treatment temperature is 200 degrees C - 1200 degrees C, and, as for heat treatment time amount and a heat treatment ambient atmosphere, it is desirable to select the optimal conditions suitably and to perform them. the case where the above-mentioned heat treatment is performed to the permanent magnet which performed aging treatment beforehand -- 200degree-C- it is desirable to heat-treat in the range below the aging treatment temperature concerned. This is to lose the aging treatment effectiveness given in advance, and for magnetic properties to fall, when heat treatment exceeds aging treatment temperature. Furthermore, after performing heat treatment beyond the aging treatment temperature concerned, it is also possible to perform aging treatment or to perform aging treatment to heat treatment and coincidence.

[0017]

[Function] By exposing a rare earth magnet into the ambient atmosphere containing the inside of a fluorine system gas ambient atmosphere, or fluorine system gas, and carrying out fluorination processing, by making the stable compound which becomes the surface of a rare earth magnet from RF3 compound, a ROXFY compound, or the mixture of both that compound form, or performing further necessary heat treatment, this invention can promote the eburnation of this compound, and stabilization further, and can raise the corrosion resistance of a rare earth magnet remarkably. Moreover, since the fluorination processing by this invention is the gaseous-phase-solid phase reaction of fluorine system gas (gaseous phase) and a rare earth magnet (solid phase) Since there is almost no elution of a magnet raw material during processing and the problem of residuals, such as an acid solvent by the so-called wet processes; such as electrolysis plating and nonelectrolytic plating, and an alkali solvent, can be solved further, The effectiveness which was excellent also as surface treatment at the time of the prodigal corrosion resistance which burn by not carrying out being acquired, and carrying out surface treatment especially of the surface treatment is demonstrated.

[0018]

[Example]

The sample which performed the whole surface grinding process to the R-T-B system sintering permanent magnet with which a presentation consists of the 31.5BND1.15 remainder Fe (% of the weight) as example 1 sample After inserting into the container which can carry out pumping and carrying out evacuation of the inside of this container to 10 to 5 or less mmHgs, Introduce the mixed gas (10% F<sub>2</sub> or 90% N<sub>2</sub>, 99.9% of purity) of F<sub>2</sub> and N<sub>2</sub> in a 10-2mmHg container, and fluorination processing which leaves a sample for 10 minutes is performed. The magnet by this invention that formed RF3 compound and a ROXFY compound, or the mixture of both that compound in the magnet surface section was obtained (sample No.1). When the thickness of the compound formed in the above-mentioned sample was measured by EPMA, the formation thickness of a compound was about 10 micrometers. Moreover, the P.C.T trial (the temperature of 125 degrees C, 85% of humidity, pressure 2atm) of the above-mentioned sample was performed on the conditions of 12 hours and 120 hours, and the comparison of the weight variation by the oxidation after a trial estimated corrosion resistance. The result of a trial is shown in a table 1.

[0019] In the sample which processed it into the R-T-B system sintering permanent magnet of example 2 example 1 and this presentation After performing the same fluorination processing as an example 1 and carrying out evacuation to 10 to 5 or less mmHgs, After heating the inside of this container in temperature of 400 degrees C and holding it for 60 minutes, the magnet by this invention that formed RF3 compound and a ROXFY compound, or the mixture of both that compound in the magnet surface section was obtained (sample No.2). When the thickness of the compound formed in the above-mentioned sample was measured by EPMA, the formation thickness of a compound was about 10 micrometers. Moreover, the P.C.T trial same in the above-mentioned sample as an example 1 is performed, and the result of having evaluated corrosion resistance by the comparison of the weight variation by the oxidation after a trial is shown in a table 1.

[0020] The sample which processed it into the R-T-B system sintering permanent magnet of example 3 example 1 and this presentation After inserting into the container which can carry out pumping and carrying out evacuation of the inside of this container to 10 to 5 or less mmHg, Heat the inside of this container in temperature of 200 degrees C, and NF<sub>3</sub> (3 nitrogen fluoride: 99.9% of purity) is further introduced in a 10-4mmHg container. After performing fluorination processing which leaves a sample for 30 minutes, 400 degrees C and heat treatment for 60 minutes are performed under the vacuum ambient atmosphere of 10 to 5 or less mmHg. The magnet by this invention that formed RF<sub>3</sub> compound and a ROXFY compound, or the mixture of both that compound in the magnet surface section was obtained (sample No.3). When the thickness of the compound formed in the above-mentioned sample was measured by EPMA, the formation thickness of a compound was about 5 micrometers. Moreover, the P.C.T trial same in the above-mentioned sample as an example 1 is performed, and a test result is shown in a table 1.

[0021] The sample which processed it into the R-T-B system sintering permanent magnet of example 4 example 1 and this presentation After inserting into the container which can carry out pumping and carrying out evacuation of the inside of this container to 10 to 5 or less mmHg, Heat the inside of this container in temperature of 400 degrees C, introduce CF<sub>4</sub> (4 methane fluoride: 99.9% of purity) in 10mmHg containers further, and fluorination processing which leaves a sample for 10 minutes is performed. The magnet by this invention that formed RF<sub>3</sub> compound and a ROXFY compound, or the mixture of both that compound in the magnet surface section was obtained (sample No.4). When the thickness of the compound formed in the above-mentioned sample was measured by EPMA, the formation thickness of a compound was about 20 micrometers. Moreover, the P.C.T trial same in the above-mentioned sample as an example 1 is performed, and a test result is shown in a table 1.

[0022]-After processing it into the R-T-B system sintering permanent magnet of example 5 example 1 and this presentation, The sample which performed 500 degrees C and aging treatment for 60 minutes is inserted into the container which can carry out pumping. After performing fluorination processing which leaves a sample for 1 minute in the ambient atmosphere made to \*\*\*\* HF (hydrogen fluoride: 99.9% of purity) after carrying out evacuation of the inside of this container to 10 to 5 or less mmHg, 500 degrees C and heat treatment for 60 minutes were performed under the vacuum ambient atmosphere of 10 to 5 or less mmHg, and the magnet by this invention that formed RF<sub>3</sub> compound and a ROXFY compound, or the mixture of both that compound in the magnet surface section was obtained (sample No.5). When the thickness of the compound formed in the above-mentioned sample was measured by EPMA, the formation thickness of a compound was about 100 micrometers. Moreover, the P.C.T trial same in the above-mentioned sample as an example 1 is performed, and a test result is shown in a table 1.

[0023] What does not perform fluorination processing at all only by performing sintering post processing to the R-T-B system sintering permanent magnet which the thing (sample No.6) which does not perform fluorination processing at all, and the presentation consisted of the Nd<sub>31.5</sub>B<sub>1.15</sub>Co<sub>5.0</sub> remainder Fe (% of the weight), added Co to the same R-T-B system sintering permanent magnet of a presentation as the example example of a comparison, and raised the corrosion resistance of a raw material beforehand only by performing sintering post processing to it (sample No.7) was obtained. The P.C.T trial same about the sample of the above-mentioned example of a comparison as an example 1 is performed, and a test result is shown in a table 1.

[0024]

[A table 1]

	試料No.	重量変化量 ( $\Delta/\text{cm}^2(\times 10^{-4})$ )	
		P.C.T試験 12時間後	P.C.T試験 120時間後
実 施 例	1	0.0	0.9
	2	0.0	0.0
	3	0.0	0.0
	4	0.0	0.5
	5	0.0	0.0
比 較 例	6	18.6	24.0
	7	2.5	4.7

[0025] Under a severe environment like a P.C.T trial, oxidation advances remarkably with the passage of time, and the magnet (sample No.6) which does not perform fluorination processing has a sharp change of weight so that clearly from a table 1. Moreover, even if it is the magnet (sample No.7) which raised the corrosion resistance of a raw material beforehand by addition of Co, oxidation is advancing with the passage of time and corrosion resistance is inferior. On the other hand, it turns out that it has the outstanding corrosion resistance, without the rare earth magnet (sample No.1-5) by this invention that performed fluorination processing oxidizing under a very severe situation also about which thing which performed fluorination processing on condition that versatility. It turns out that especially the magnet (3 sample No.2, 5) that performed heat treatment after performing fluorination processing does not have weight change which approaches a P.C.T trial, and it has the extremely excellent corrosion resistance. This is because RF3 very stable compound and a ROXFY compound, or the mixture of both that compound is formed in the surface section of a rare earth magnet which performed fluorination processing by this invention to moisture etc.

[0026] Moreover, after performing fluorination processing in the ambient atmosphere which contains fluorine system gas according to the magnet (sample No.1) and example 2 which performed fluorination processing in the ambient atmosphere which contains fluorine system gas according to an example 1, the X diffraction (Cu-kalpha is used for a target) of the magnet surface section was performed about each of the magnet (sample No.2) which heat-treated further. The result of an X diffraction is shown in drawing 1 with the result about the unsettled magnet (sample No.6) which does not perform fluorination processing at all. In addition, A of drawing 1 shows example 2 magnet of sample No.2, and, as for B, example 1 magnet of sample No.1 and C show the result of the X diffraction of an unsettled magnet (sample No.6). About the unsettled magnet (sample No.6) which does not perform fluorination processing, it turns out that Nd<sub>2</sub>Fe<sub>14</sub>B which are the configuration layer of this magnet, and Nd exist so that clearly from drawing 1. These Nd<sub>2</sub>Fe<sub>14</sub>B and Nd(s) tend to oxidize very easily like point \*\*, once an oxide is formed, since those oxides are hygroscopicity, they will react with the moisture in atmospheric air easily in a magnet front face, and degreining of the magnet configuration phase which makes a lifting and R<sub>2</sub>Fe<sub>14</sub>B phase the start for cubical expansion, and omission are caused. On the other hand, about what performed heat treatment (sample No.2), it turns out that the compound of the

rare earth elements with which the whole makes the subject mostly mixture of NdF<sub>3</sub> and NdOF, or both its compound, such as above Nd, and the fluorine of the magnet surface section exists after the thing (sample No.1) which performed fluorination processing, and fluorination processing. Like the above, by heat-treating to the Ushiro pan which performed fluorination processing to the rare earth magnet, or performed fluorination processing, the rare earth which has an adverse effect especially on corrosion resistance among rare earth magnet configuration phases, its oxide, etc. can be used as the compound of the rare earth elements which make a subject mixture of NdF<sub>3</sub>, NdOF, or both its compound, and a fluorine, and the corrosion resistance of the raw material of a rare earth magnet itself can be raised substantially.

[0027]

[Effect of the Invention] This invention can raise substantially the corrosion resistance of the raw material of a rare earth magnet itself by performing fluorination processing into the ambient atmosphere which contains the inside of a fluorine system gas ambient atmosphere, or fluorine system gas in a rare earth magnet, and making the mixture which becomes the surface section of a rare earth magnet from RF<sub>3</sub> stable compound, a ROXFY compound, or both its compound to corrosion resistance form, or performing further necessary heat treatment. Moreover, since the processing itself is dramatically easy and it is moreover the gaseous-phase-solid phase reaction of fluorine system gas (gaseous phase) and a rare earth magnet (solid phase), the fluorination processing by this invention Since the corrosion resistance of the rare earth magnet raw material itself can be improved in there being almost no elution of a magnet raw material during processing and being able to solve the problem of residuals, such as an acid solvent by the so-called wet processes, such as electrolysis plating and nonelectrolytic plating, and an alkali solvent, further, Even if it demonstrates the effectiveness which was excellent also as surface treatment at the time of carrying out surface treatment and does not perform further especially surface treatment, it becomes possible to use a rare earth magnet under a cruel environment.

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[Translation done.]